C.D.Kochakian

BOSTON UNIVERSITY

GRADUATE SCHOOL

Thesis

NEW EXPERIMENTS FOR A LABORATORY COURSE IN ORGANIC CHEMISTRY

by

Charles Daniel Kochakian

(A.B., Boston University, 1930)

submitted in partial fulfilment of the
requirements for the degree of
Master of Arts

1931

BOSTON UNIVERSITY
COLLEGE OF LIBERAL ARTS
LIBRARY

p6923

upstairs
378.744
BO
A.M. 1931
koc

THE CATALYTIC PREPARATION OF ACETONE FROM ACETIC ACID

I. Introduction 2

II. The Development of the Experiment 3

  A. Preparation of the catalyst 3

  B. The development of a uniform heating system 5

  C. The development of apparatus and procedure 6

  D. The determination of optimum temperature and the optimum time 8

  E. The reaction is a case of dehydration 10

III. Summary 12

Diagram 11 a

THE CATALYTIC PREPARATION OF ACETONE FROM ACETIC ACID

Laboratory methods for the preparation of acetone have not kept pace with the commercial methods. In the average college laboratory acetone is prepared by the dry distillation of calcium acetate. This method however, has been abandoned by industrial manufacturers and among other methods a catalytic process has been substituted by means of which acetic acid is converted directly to acetone. Squibb,[1] in his experiments, found that if acetic acid was passed over calcium carbonate at a sufficiently high temperature acetone would be formed:

$$2\ CH_3\ COOH\ ---\ CH_3\ COCH_3 + CO_2 + H_2O$$

Therefore, in an attempt to devise a suitable laboratory experiment that would produce a favorable yield of acetone from acetic acid passedover a catalyst, six experiments in all were carried out.

---

[1] SQuibb - Journal of the American Chemical Society. 17,187(1895)
18,231(1896)

THE DEVELOPMENT OF THE EXPERIMENT

As a result of observations and results of the first two experiments, an efficient catalyst, a suitable means of heating, and a simple form of apparatus and procedure were developed.

A. Preparation of the Catalyst. In developing a suitable catalyst, an attempt was made to obtain a method of preparation that would give an active efficient catalyst dispersed to give a maximum surface. This was attained by a process of improvement from observations. The catalyst for the first experiment was prepared by adding the calculated amount of 50% sodium hydroxide to 500 cc. of a 10% solution of calcium nitrate in which 12 grams of shredded asbestos had been dispersed. Thus the precipitated calcium hydroxide became thoroughly mixed and absorbed in the asbestos to provide a maximum surface. The mixture was filtered, washed, and dried. The catalyst mixture was then placed in the combustion tube and heated for about one hour to change the hydroxide to the oxide.

In preparing the catalyst for the second experiment, a different means of obtaining the oxide was employed. The catalyst was prepared by precipitating calcium carbonate by the

Digitized by the Internet Archive
in 2016

https://archive.org/details/newexperimentsfo00koch

addition of a 15% solution of sodium carbonate to a 15% solution of calcium nitrate containing shredded asbestos. Then the dried catalyst was placed in the combustion tube and heated for one to two hours to decompose the carbonate to the oxide. Analysis at the end of the experiment showed that the decomposition was not complete.

The third and final method for the preparation of the catalyst was deemed adequate and more efficient than the previous two. 15-20 grams of pumice, broken to pieces the size of a bean, and 10 grams of shredded asbestos were placed into 500 cc. of a 10% solution of calcium nitrate, to which was added the calculated amount of 15% sodium carbonate solution slowly and with good stirring. The resulting mixture was filtered and washed. Next a batch of calcium carbonate was made from 1000 cc. of a 10% solution of calcium nitrate. This last pasty mass of just calcium carbonate was mixed thoroughly with the first moistened mixture and dried. The entire mixture then was placed in an evaporating dish and heated in a brick oven at the highest temperature possible by means of the blast flame for about two hours in order to decompose the calcium carbonate completely to calcium oxide.

The mixture was then placed in the combustion tube with a layer of four inches of broken pumice at each end.

B. The Development of a Uniform Heating System:

In conjunction with the preparation of a catalyst, a means of uniform heating was attained. The main difficulty of an experiment that requires a high temperature is not only to attain the desired temperature but to maintain the temperature constantly at a uniform rate over the desired period of time. This was successfully accomplished after three trials.

In the first trial an improvised furnace of asbestos sheeting was constructed. A piece of asbestos about the length of the tube was rolled to form a cylinder about twice the diameter of the combustion tube. Two slits were made in the cylinder; through the bottom slit, the flames of three Bunsen burners were introduced; the top slit acted as a vent for the flames. This initial attempt was unsatisfactory for not only did the temperature fluctuate but it could not be regulated.

In the second experiment modifications were made which were hoped to give the desired results. The furnace of asbestos was discarded and five wing top burners connected to

one gas supply by means of three way glass tubing were used. Although this method proved better than the first, it was not, however, suitable.

These two trials indicated that other means of heating ought to be employed. Electricity as a means of heating using a resistance coil of nichrome wire was found satisfactory. In order to obtain an efficient furnace, capable of producing a satisfactory temperature, several coils had to be made until a coil of the necessary length was found. Three strips of thin asbestos were placed along the combustion tube and around these strips were wound about 20 feet of nichrome wire (resistance 1.64 ohms per foot) and the whole was insulated by three folds of heavy asbestos which was moistened and molded to a compact mass. This furnace was capable of heating to 700° C.which was, however, higher than necessary. Therefore, a rheostat of suitable resistance was placed in series with the furnace. Any desired temperature, thus could be maintained uniformly.

C. The Development of the Apparatus and the Procedure.

At the same time that a suitable catalyst, and a means of uniform heating were being developed, a method of procedure

and a suitable form of apparatus were also being developed. The procedure was always essentially the same. The apparatus however, was slightly modified. During the development of the final form of the apparatus, a carbon dioxide waste bottle which was placed after the water bottle was omitted, for no analysis was to be made for carbon dioxide. Secondly, the system at first was connected to a water pump by means of which a slight **decrease in** pressure was obtained to secure forward action, but it was found that the **vapors were** capable of forward movement without external aid. In the method as finally devised, glacial acetic acid was vaporized in a round bottom flask and **passed** through a combustion tube containing the catalyst heated to about 500° C. by means of nichrome resistance wire. Here the acetic acid was converted to acetone. The hot vapors from the combustion tube were led to a 500 **cc.** flat bottom flask which acted as an air condenser, liquefying any unconverted acetic acid and some acetone. The remaining vapors consisting of acetone, carbon dioxide, and some methane, were led to a water condenser which was attached to an Erlenmeyer flask immersed in ice, where practically all of the acetone liquefied. A small amount of acetone escaped condensation which was absorbed, however, in a water bottle. The remaining gases - carbon dioxide and methane - were allowed to escape.

D. The Determination of Optimum Temperature and the Optimum Time.

Now that a suitable catalyst, uniform heating, and a satisfactory procedure and apparatus had been attained, an experiment was run to test the methods as developed and to determine at the same time the temperature at which best results could be obtained. Then two more experiments were run to determine the optimum rate of passage of acetic acid aver the catalyst.

In the first experiment 93 cc. of glacial acetic acid was passed through in one hour at a temperature of 500 - 525° C. (29.5 - 30.5 millivolts). When the passage of acetic acid was stopped, the flask was removed, the end of the combustion tube stoppered, and heating was continued for ten minutes with slowly increasing temperature. In the meantime the vapors were tapped at the stoppered end and a match applied; a flame resulted which became gradually more intense with the rise in temperature indicating the formation of methane. This experiment was quite satisfactory. The flask in the ice bath contained 34.5 cc. of clear liquid which on fractionation yielded 28.5 cc. of distillate boiling at 55 - 56.5° C.[1], and

---

[1] Boiling point of Acetone - 56.5° C

a specific gravity of 0.797 $\frac{20}{20}$[1], left a residue of 4 cc, and a loss of 2 cc. by evaporation. The air condenser contained 28.5 cc. of liquid which on fractionation yielded 3.5 cc. of distillate collected at 56° C, 23.5 cc. of residue, boiling at about 100° C, and a loss of 1.5 cc. The water bottle contained approximately 3 cc. of acetone. Thus, a total yield of about 60% of acetone was obtained.

In the next trial 94 cc. of acetic acid **was passed** over a new charge of the same mixture of catalyst in about two hours at a slightly lower temperature than the previous experiment, the temperature varying from 460 - 500° C (27 - 30 millivolts). **Also a modification was made,** in the apparatus. A water bath heated to 60° C. was placed under the air condenser to prevent the condensation of acetone there. The yield in this experiment was about 70%. The flask in the ice bath contained 56 cc of a yellowish liquid which on fractionation yielded 40 cc of acetone **boiling** at 56° - 57° C and **having** a specific gravity of 0.809 $\frac{20}{20}$. The air condenser contained 8.5 cc. of liquid which on fractionation at 56° C yielded 0.5 cc. of acetone. A comparatively insignificant amount. The wash bottle contained 2.5 cc. of acetone as estimated by the benzaldehyde reaction.

---

[1] Specific gravity of acetone - 0.792 $\frac{20}{20}$

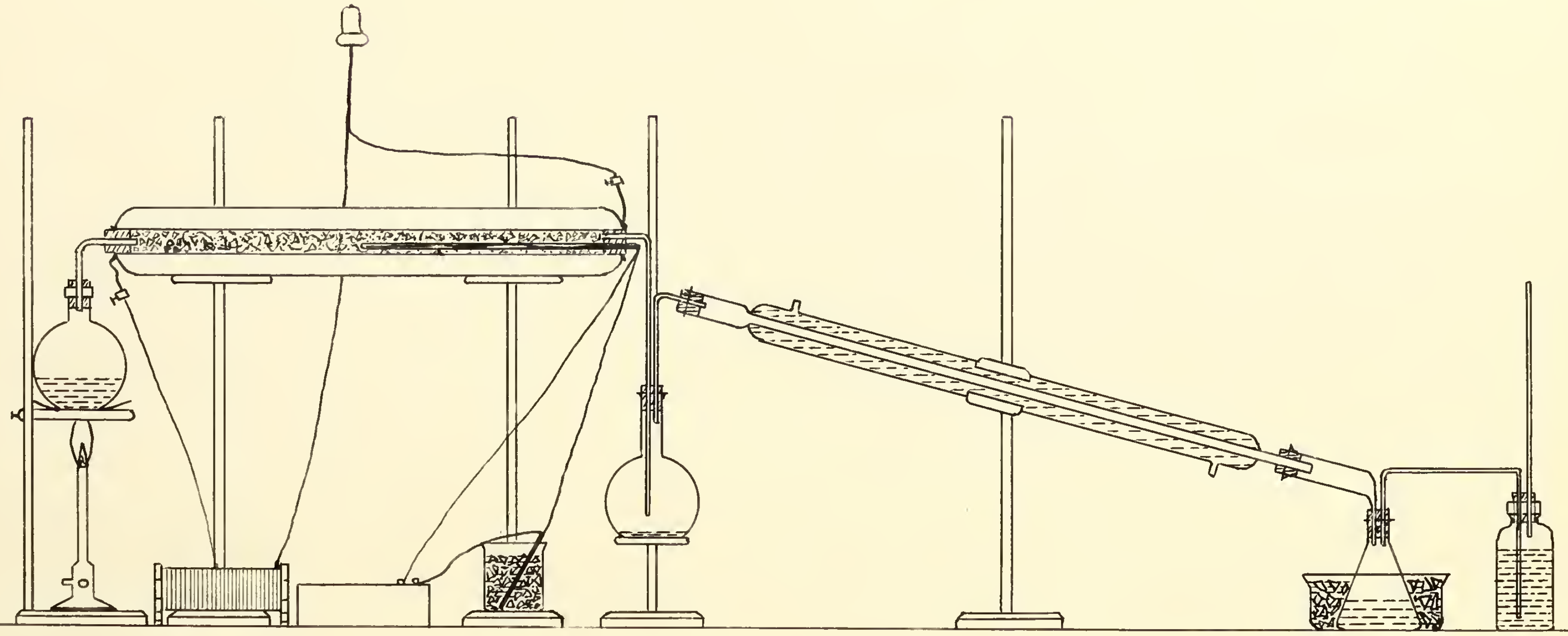
Immediately after the above experiment another experiment was run without replacing the catalyst. In this case 96 cc. of acetic acid was passed over in the short time of 30 minutes at a temperature of 490° C.(29 millivolts). The yield, 60%, , was large enough to warrant the saving of the time. The flask in the ice bath contained 45 cc. of a yellowish liquid which yielded 33 cc. of acetone boiling at 55°- 57° C and a specific gravity of $0.808\frac{20}{20}$. The air condenser contained 4.5 cc of liquid which yielded 1 cc of acetone. The water bottle contained about 1.5 cc. of acetone as estimated by the benaaldehyde reaction.

After the experiment the apparatus was dismantled and a physical examination of the catalyst was made. A deposit of carbon sufficient to give the catalyst a gray-black coloration was found.

E. The Reaction is a Case of Dehydration. The deposit of carbon ought to "poison" the catalyst to some extent, although there is no conclusive proof that it has any serious effects on the results. If the carbon on the other hand does not affect the catalyst, it is probable that the reaction is only a surface reaction. This bit of speculation was put to experiment. Small pieces of pumice and shredded asbestos were

mixed together to serve as a catalyst. An experiment was run yielding methane, carbon dioxide, and a trace of acetone which were evidently due to pyrolysis. This experiment proved quite conclusively that the reaction is a case of dehydration and not just a surface reaction.

Apparatus for the Catalytic Preparation of Acetone



Scale 1.5" = 1'

SUMMARY

As a result of this study of the catalytic preparation of acetone, a sufficiently simple laboratory method has been developed which is capable of satisfactory results. The catalyst mixture is prepared according to the directions on Page 3 and is treated in the brick oven just prior to using. While the catalyst is being decomposed, the apparatus is set up as in the diagram. All the connections are made tight except the ones on the combustion tube. The combustion tube is brought to the required temperature, 475 - 500° C.(27 - 30 millivolts) by means of a rheostat (Page 6); using a chromel-copel thermocouple connected to a millivoltmeter which has been calibrated against a potentiometer to read the temperature. When the catalyst mixture is sufficiently heated (page 4), it is allowed to cool so that the evaporating dish containing the mixture may be comfortably handled with tongs, and the catalyst is then placed in the combustion tube. The stopper containing the thermocouple is inserted, enough pieces of pumice are placed in the tube to form a four inch layer, the catalyst mixture is added to within five inches of the end, and the rest filled with pieces of pumice. The combustion tube is now put in position, the flask containing

the acetic acid attached, and when the required temperature is again attained, the acid is vaporized at such a rate that 100 cc. passes over in 45 - 60 minutes. When almost all of the acid is vaporized, the flask is removed, the end of the combustion tube stoppered and the temperature is allowed to remain at 500° C for about 10 minutes longer. Then the current is shut off and the acetone is purified by fractional distillation. The flask in the ice bath contains the bulk of the acetone which is obtained by distilling with an efficient fractionating column, collecting the portion boiling up to 56.5° C. The air condenser contains mostly unconverted acetic acid, a tarry by-product, and a little acetone which can be obtained by distilling with an efficient fractionating column. A yield of at least 60% should be obtained.

THE PREPARATION AND IDENTIFICATION OF

BUTYL PHENYL CARBINOL

I. Introduction 15

II. Preparation 16

III. Identification 19

A. Physical Properties 19

1. Boiling point

2. Index of Refraction

B. Derivatives 20

1. Phenylhydrazone 21

2. 2.4 dinitro phenyl hydrazone 21

3. p-nitrophenylhydrazone 22

IV. Summary 23

THE PREPARATION AND SOME DERIVATIVES OF
BUTYL PHENYL CARBINOL

The Grignard reaction is a common method of synthesis in Organic chemistry. The original work of Grignard for whom the reaction has been named has been supplemented and extended by many other researchers. Among the researchers of recent times, Henry Gilman and his co-workers have perhaps done the most work on the Grignard reaction. Their results,[1] therefore, are employed in the preparation of butyl phenyl carbinol which was found convenient to prepare because the reactants - butyl bromide and benzaldehyde - are relatively inexpensive and readily obtainable. No information concerning the compound, however, could be found in the available literature. The compound evidently has not been prepared before and the only related compound that could be found was butyl phenyl **ketone**[2] for which, however, no means of identification excepting the boiling point was available. As a result the properties of butyl phenyl carbinol had to be determined by experiment.

---

[1] Henry Gilman, and Charles H. Meyers - "A Study of the Optimum Conditions for the Preparation of Ethyl Magnesium Bromide" - Journal of American Chemical Society 45,156, 159-165 (1923)

[2] Samuel P. Mulliken - "The Identification of Pure Organic Compounds", Volume I, p. 144. John Wiley & Sons, N.Y., 1904.

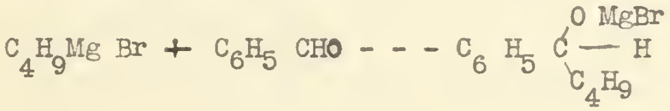
PREPARATION

48.6 grams (2 moles) of clean dry magnesium turnings and 350 cc. of ether were placed in a clean dry 5-liter flask fitted with a mechanical stirrer, a clean dry separatory funnel, and an efficient clean dry reflux condenser. Then 274 grams (2 moles) of butyl bromide mixed with 450 cc. of anhydrous ether was added slowly by means of the separatory funnel. The stirrer was started and the bottom of the flask was slightly warmed to induce reaction (a crystal of Iodine will also induce reaction). In about 5 minutes the reaction was evident by bubbles appearing on the turnings and the mixture of butyl bromide and ether was added at a rate to produce gentle boiling. After all the butyl bromide was added (1 hour and 45 minutes) the stirring was continued for 15 minutes to insure completion of the reaction. All of the magnesium did not react. The unreacted magnesium, however, has no effect on the final results.

$C_4H_9Br + Mg$ - - - C_4H_9MgBr

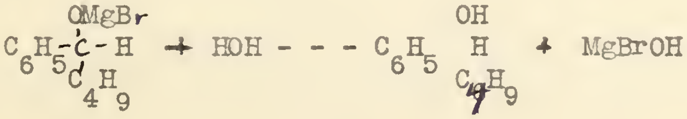
When the preparation of the Grignard Reagent was complete, 190.8 grams (1.8 moles) of freshly distilled benzaldehyde mixed with 200 cc of anhydrous ether was added in 1 hour and 15 minutes. The reaction took place with the evolution of con-

siderable heat; therefore the benzaldehyde was added slowly and the flask was cooled with an ice-salt mixture. After all the benzaldehyde was added, .5 cc - 1 cc of the reaction mixture was removed and a test made to detect any uncombined Grignard reagent.[1] Since the test was positive, the stirring was continued for 15 minutes longer with the removal of the cooling mixture, when the test was negative.



$$C_4H_9MgBr + C_6H_5CHO - - - C_6H_5\,\overset{OMgBr}{\underset{C_4H_9}{C}} - H$$

Next the addition product was hydrolyzed with good cooling. 98 grams (1-mole) of concentrated sulfuric acid dissolved in 2 liters of water was added slowly for the first ten minutes when the heat of reaction was greatest and then the rate was increased rapidly so that the complete process took 45 minutes. The precipitated magnesium hydroxide did not dissolve immediately and the stirring had to be continued for approximately one hour more before all the $Mg(OH)_2$ dissolved.

1. 

$$C_6H_5 - \overset{OMgBr}{\underset{C_4H_9}{C}} - H + HOH - - - C_6H_5\,\overset{OH}{\underset{C_4H_9}{H}} + MgBrOH$$

2. $2MgBrOH + H_2SO_4 - - - MgBr_2 + MgSO_4 + 2\,HOH$

---

[1] Henry Gilman and F. Schulze - "A Qualitative Color Test for the Grignard Reagent." - Journal of American Chemical Society, 47, 2002 - 2005 (1925).

When the hydrolysis was complete the ether layer was separated from the water layer, washed twice with sodium bicarbonate to remove any traces of acid, and twice with water to remove any sodium bicarbonate, and then dried with fused potasium carbonate. When the mixture was dry, it was filtered and distilled on a water bath to remove the ether. The remaining liquid (257.3 grams) containing a trace of benzaldehyde gave 87.2% yield of the crude product, which was fractionated at a pressure of 5 mm and the portion boiling at 113.5 - 115° C was collected as the pure product netting a yield of 59.8% which could be considerably increased by refractionating the first portion but the time and effort required did not warrant it.

IDENTIFICATION

A. Physical Properties:

1. Boiling Point. An attempt was made to distill the carbinol at atmospheric pressure, so that not only could the product be obtained easily in a pure state, but also that the true boiling point might be determined. The baths used, however, did not prove very convenient or satisfactory. First a bath of concentrated H_2SO_4 and $KHSO_4$ was employed. This bath proved unsatisfactory and very dangerous for it could not be safely heated to the temperature required for the distillation. Next a metal bath of a entectic mixture of lead and tin was employed to determine the boiling point. Superheating in this case was too great and consequently no true boiling point could be obtained. Therefore, vacuum distillation was resorted to as the most convenient and satisfactory method. The boiling point by this method was 115.1° C at 5 mm pressure. A micro boiling point was also obtained, 248 - 250° C (u.c.)

2. Index of Refraction. In order to determine when the pure product was obtained, four fractions were collected. The first fraction (83.2 grams) boiling

up to 113.5° C. had an index of refraction of 1.5111, the second fraction (66.5 grams) boiling at 113.5 - 115° C. had an index of refraction of 1.5100. The third fraction (68.1 grams), boiling at 115° C had an index of refraction of 1.5091 and the fourth was identical to the third. All the readings were taken at approximately the same temperature, that of the laboratory, 24.6° C. Therefore the index of refraction of butyl phenyl carnibol of 24.6° C. is 1.5096.

B. Derivatives: Several attempts were made to prepare solid derivatives of butyl phenyl carbinol with the different alcohol reagents - 3 nitro phthal~~l~~ic anhydride, phenyl isocyanate, benzoyl chloride, acetyl chloride. Since satisfactory derivatives of the carbinol could not be obtained, it was oxidized to butyl phenyl ketone and derivatives of this compound were obtained. 5 cc. of the carbinol was refluxed for one hour with 15 grams of sodium dichromate dissolved in 100 cc. of water and 25 cc. of concentrated sulfuric acid dissolved in 250 cc. of water, The ketone was separated, by means of a separatory funnel. The ketone contained some of the inorganic salts which could not be removed, but the preparation of derivatives was not noticeably affected by the impurities.

2. Phenylhydrazone[1]. 0.5 cc. of the ketone was dissolved in 2 cc. of alcohol. Then water was added drop by drop until the precipitate first formed just redissolved. To the clear solution was added 0.5 cc of phenylhydrazine and after a few minutes a drop or two of glacial acetic acid. The mixture was allowed to stand until crystallization was complete. The crystals were filtered under suction and then recrystallized several times from dilute alcohol and finally dried under suction. The crystals obtained were white. Three successive melting points were taken, yielding the following results, 72.7° C, 72.1° C, and 71.6° C. This abnormality could not be accounted for at first. However, the crystals were placed in the dessicator to dry completely, and when observed after 20 minutes, the crystals had become yellow and on further standing completely disappeared. Therefore, the phenylhydrazone of butyl phenyl ketone is unstable at ordinary conditions.

2. 2 ,4 dinitrophenylhydrazone[2] : 1 gram of 2,4 dinitrophenylhydrazine and 1.2 cc. of butyl phenyl ketone in 50 cc. of alcohol were heated to boiling on a water bath, allowed to cool slightly and 1 cc. of conc HCl added. A precipitate appeared almost immediately. After boiling for 2

[1] "Qualitative Organic Analysis" - Oliver Kamm, John Wiley and Sons Inc. P. 143 (1930).

[2] "The Identification of Carbonyl Compounds by Use of 2,4 dinitrophenylhydrazine." - Journal of American Chemical Society. 52, 2955 (1930).

minutes, the solution was set aside until crystallization was complete, filtered by suction, washed with alcohol, and recrystallized to constant melting point. The crystals were red-orange and melted sharply at 163.5° C (u.c.).

The nitrogen content obtained by the Kjeldahl method as modified by Dafert[1] checked with the calculated value.

3. p-nitrophenylhydrazone. 0.4 gram of p-nitrophenylhydrazine and 15 cc. of alcohol were heated on a water bath until the p-nitrophenylhydrazine dissolved, then 1 cc. of the ketone was added and the solution set aside to crystallize. After about 1 hour, 7 cc. of water was added, and a yellow precipitate resulted which on standing settled out as yellow-brown crystals, which were filtered, dried under suction, and recrystallized from alcohol to constant melting point. The yellow brown crystals melted sharply at 125° C. (u.c.).

A nitrogen determination by a semi-micro[2] Kjeldahl method checked favorably with the calculated value.

---

[1] "Organic Laboratory Methods" - Professor Lassar-Cohn. Translation by Ralph E. Oesper. P. 420. Williams & Wilkins Company, 1928, Baltimore.

[2] "The Identification of Carbonyl Compounds by the use of 2,4 dinitrophenylhydrazine." - Journal American Chemical Society 52, 2955. July 1930.

SUMMARY

As a result of this study of the preparation and identification of butyl phenyl carbinol, it is believed that a suitable laboratory method for the carrying out of the Grignard reaction has been obtained, and also that the product formed although not directly identified in all cases has been satisfactorily identified in a simple manner.

BOSTON UNIVERSITY

1 1719 02574 1895